EVALUATION OF AZINPHOS-METHYL AS A TOXIC AIR CONTAMINANT

$$\begin{array}{c} S \\ H_3C-O \\ H_3C-O \end{array} = \begin{array}{c} O \\ P-S-CH_2-N \\ N \\ N \end{array}$$

Part A

Environmental Fate



California Environmental Protection Agency Sacramento, California

November 1999

California Environmental Protection Agency Department of Pesticide Regulation

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Part A

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November 1999

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I. Background

Legislation passed in 1983 and 1984 established a regulatory framework for the identification and control of toxic air contaminants (TACs). Assembly Bills 1807 and 3219, referred to collectively as AB 1807, mandate that the Department of Pesticide Regulation (Food & Agr. Code, § 14021 et seq.) and the Air Resources Board (Health and Saf. Code, § 39650 et seq.) declare and regulate TACs "...which may pose a present or potential hazard to human health". The Air Resources Board (ARB) is responsible for regulating TACs in their industrial applications. The Department of Pesticide Regulation (DPR) has jurisdiction over the regulation of the use of pesticides in the production of food, fiber, forest products, ornamental horticulture, and other uses that include structure, home, and landscape maintenance.

Pursuant to the requirements of AB 1807, DPR may request ARB to monitor concentrations of a pesticide in both the ambient community air and near pesticide applications. In making these requests, DPR outlines the physical/chemical characteristics of the pesticide, describes use patterns, and includes monitoring recommendations that pinpoint commodities, counties, and seasons where highest use occurs. DPR uses the resulting monitoring data along with data from prior air monitoring studies and toxicological data to produce a health effects document that contains 1) Part A—a summary of the monitoring recommendation, the results of the ARB monitoring studies, and a review of the physical/chemical properties and environment fate of the candidate pesticide; 2) Part B—an estimate of the levels of exposure in air that may cause or contribute to adverse health effects; and 3) Part C—an estimate of the potential human health risk resulting from those exposures. This document is subsequently reviewed by ARB, the Office of Environmental Health Hazard Assessment, the Department of Health Services, the Scientific Review Panel, the pesticide registrants, and the public. Following review and acceptance by the Scientific Review Panel, the health effects document becomes the basis for the determination of whether the candidate is a potential threat to human health and should be declared a TAC. If a pesticide is identified as a TAC, DPR determines the need for and degree of control measures to reduce public exposure. Control measures may include label amendments, applicator training, restriction on use patterns or locations, changes in application procedures, cancellation of registration, and reclassification as a restricted material. The use of a restricted material is governed by regulations which prescribe the time when and the conditions under which use or possession may occur so that there is no danger or hazard to public health, the environment, animals, or crops.

II. Chemical Description

Azinphos-methyl

Common Name: azinphos-methyl

Chemical Names: O,O-dimethyl S[(4-oxo-1,2,3-benzotriazin-

3(4H)-yl)methyl] phosphorodithioate

S-(3,4-dihydro-4-oxobenzo[d]-1,2,3]-triazin-

3-ylmethyl) O,O-dimethyl phosphorodithioate

Trade Names: Gulthion®, Gusathion® (Bayer); Gowan Azinphos-M 2EC,

Gowawn Azinphos-M 2EC, Gowan Azinphos-M 50 WSB (Gowan);

Azinphosmethyl 50W Soluble (Micro-Flo)

CAS Registry Number: 86-50-0

Molecular Formula: C10H12N3O3PS2

Molecular Weight: 317.33

Figure II-1. Chemical structure of azinphos-methyl

$$H_3C \longrightarrow O$$
 $P \longrightarrow S \longrightarrow C$
 H_2
 N
 N

Azinphos-methyl (Figure II-1) is a non-systemic insecticide/acaricide belonging to the broad chemical class of organophosphorus (OP) compounds. OPs, characterized by the structure shown in Figure II-2a, are derived from the inorganic acids of phosphorus. More specifically, azinphos-methyl belongs to the class of OPs that are derivatives of thiophosphoric acids (Figure II-2b). A sulfur atom has been substituted for one of the oxygens of the parent compound (Considine, 1984).

Figure II-2. Generalized chemical structures

$$R_1 \longrightarrow 0$$
 $R_2 \longrightarrow 0$
 $R_2 \longrightarrow 0$
 $R_2 \longrightarrow 0$
 $R_3 \longrightarrow 0$
 $R_2 \longrightarrow 0$
 $R_2 \longrightarrow 0$

(a) Organophosphorus compound

(b) Thiophosphoric acid derivative

A. Physical and Chemical Characteristics

Pure azinphos-methyl is a non-corrosive, white crystalline solid with a melting point of 74 °C. It decomposes when heated above 200 °C, and emits very toxic phosphorus, nitrogen, and sulfur oxide fumes. Azinphos-methyl photodegrades on soil and in water, and is rapidly hydrolyzed in acidic or alkaline media. It is slightly soluble in water, and soluble in common organic solvents such as benzene, xylene, methanol, and carbon tetrachloride (Budavari, 1996; British Crop Protection Council, 1994; Lewis, 1991; Montgomery, 1993; Royal Society of Chemistry, 1994; Thomson, 1997). Additional physical and chemical properties are summarized in Table II-1.

Table II-1. Physical and chemical properties of azinphos-methyl (Kollman and Segawa, 1995).

Physical/Chemical Property	Value
Water Solubility	2.80 parts per million at 20 °C
Vapor Pressure	1.60 x 10 ⁻⁶ mm Hg, 20 °C
Octanol-water Partition Coefficient (Kow)	360
Soil Adsorption Coefficient (K _{oc})	882 cm ³ /g, averaged over different soil types
Hydrolysis Half-life	19 days, at 30 °C and pH 7
Aerobic Soil Metabolism Half-life	44 days, in sand loam soil
Anaerobic Soil Metabolism Half-life	68 days, in sandy loam soil
Field Dissipation Half-life	8 days, in sandy loam soil
Henry's Law Constant (Kh)	2.55 x 10 ⁻⁸ atm-m ³ /mol, at 25 °C

B. Regulation

Azinphos-methyl was classified by the U.S. Environmental Protection Agency as a restricted use pesticide due to acute dermal and inhalation toxicity (U.S. EPA, 1986). Consequently, it was designated a restricted material pursuant to section 14005.5 of the Food and Agricultural Code. Other criteria for a restricted material designation listed in this section include posing a danger to public health, or a hazard to crops, domestic animals, farm workers, or the environment. Restricted materials are possessed and used by persons only under permit of the county agricultural commissioner.

Pursuant to section 13145(d) of the Pesticide Contamination Prevention Act (Stats. 1985, Ch. 1298, § 1), azinphos-methyl is on the Ground Water Protection List, section 6800(b) of Title 3, California Code of Regulations. Pesticide active ingredients on this list have been identified as having the potential to pollute ground water.

The Birth Defect Prevention Act (Stats. 1984, Ch. 669, § 1) mandates the listing of azinphos-methyl in section 6198.5 of Title 3, California Code of Regulations. The 200 priority pesticide active ingredients listed in this section are suspected of being hazardous to people, and have widespread use and significant data gaps.

C. References

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III. Application Methods and Use Patterns

Azinphos-methyl is a nonsystemic insecticide used to control sucking and chewing insects on a wide variety of fruits, field crops, vegetables, ornamentals, and nuts. It is available in emulsifiable concentrate, wettable powder, and wettable powder in water soluble packet or bag formulations with the Signal Word "Danger" on the product labels. As of October 1999, there were seven active registrations for products containing azinphos-methyl.

A. Application Methods

Azinphos-methyl is applied to soil or foliage by aerial or power-operated ground sprayers. It is also applied by chemigation through sprinkler, center pivot, lateral move, side roll, overhead solid set or low- pressure irrigation systems.

Application rates for field crops range from 0.125 to 0.75 pounds of active ingredient (a.i.) per acre. Respective application rates for fruit and vegetables are 0.25 - 2.0 and 0.125 - 1.5 pounds a.i. per acre. The maximum application rate for nut crops is 2.0 pounds a.i. per acre with a maximum of 3 applications per crop per season regardless of rate or formulation type.

B. Use Patterns

Full pesticide use reporting was implemented by DPR in 1990. All agricultural use must be reported monthly to the county agricultural commissioners (CACs). Agricultural use is defined as including applications to parks, golf courses, cemeteries, rangeland, pastures, and rights-of-way. The CACs forward these data to DPR, who compiles and publishes annually a Pesticide Use Report (PUR).

The annual PURs can be used to identify the counties where and the time of year a specific pesticide is most heavily used (DPR, 1998b; DPR, 1997; DPR, 1996; DPR, 1995; DPR, 1994; DPR, 1993; DPR, 1992; DPR, 1991; DPR, 1990). Table III-1 summarizes azinphos-methyl use for reporting years 1990 through 1998 by county with the counties' population (based on the 1990 census). These data indicate that, historically, more than 51 percent of azinphos-methyl use occurred in Kern, Merced, Stanislaus, and Tulare Counties during this reporting period. The total population of these four counties constitutes less than 5 percent of the total population of California. Figure III-1 is a graphical representation of the data. This figure indicates that Kern County, which accounted for nearly 30 percent of the total amount used, was the county where highest use occurred.

Table III-1. Azinphos-methyl use by county from 1990 through 1998.

	County	Pounds Applied								
County	Population ^a	1998	1997	1996	1995	1994	1993	1992	1991	1990
Butte	182,120	16,198	23,062	22,641	26,637	28,424	29,860	33,143	24,449	21,268
Colusa	16,275	2,607	3,400	2,989	2,868	1,307	4,292	5,473	2,822	2,281
Contra Costa	803,732	295	4,996	5,338	5,855	5,236	4,501	6,352	5,810	6,597
Fresno	667,490	12,326	26,109	33,380	32,866	32,226	37,330	33,730	24,065	20,462
Glenn	24,798	3,325	8,764	6,642	7,466	7,873	12,879	10,937	11,829	14,282
Kern	543,477	89,025	102,744	120,910	125,092	135,417	141,804	143,331	132,194	129,605
Kings	101,469	7,799	7,273	10,177	10,105	12,110	13,064	13,092	16,260	11,968
Lake	50,631	1,756	16,327	10,196	20,556	8,413	21,254	19,097	16,061	19,467
Madera	88,090	3,404	15,528	24,832	20,729	20,490	15,030	19,678	25,138	25,312
Mendocino	80,345	1,305	4,791	9,040	10,023	8,756	8,324	6,021	5,606	4,857
Merced	178,403	4,919	12,096	15,952	15,144	17,826	31,309	45,984	49,747	67,427
Sacramento	1,041,219	746	15,242	15,833	22,508	21,474	18,741	22,163	18,860	13,098
San Joaquin	480,628	9,084	17,920	28,311	15,697	15,246	16,769	22,443	18,781	17,707
Solano	340,421	718	3,298	3,969	5,009	6,171	6,840	6,230	7,157	7,300
Stanislaus	370,522	8,297	20,964	25,146	29,317	27,455	40,723	43,050	38,339	52,079
Sutter	64,415	1,898	6,320	7,804	5,427	5,992	8,275	12,179	7,948	8,150
Tehama	49,625	1,915	3,587	3,948	2,177	3,024	2,982	4,853	3,258	4,492
Tulare	311,921	15,772	21,140	32,161	25,026	35,063	33,759	36,738	33,063	37,155
Yolo	141,092	2,080	5,404	7,602	4,889	5,428	4,137	7,793	7,827	3,899
Yuba	58,228	2,063	9,251	10,656	10,049	5,260	7,601	11,884	9,332	16,146
All Others	24,068,020	7,776	8,139	8,538	8,780	15,721	14,817	16,066	26,314	33,655
Totals	29,662,921	193,308	336,354	406,066	406,221	418,913	474,292	520,235	484,860	517,205
^a 1990 census										

Figure III-1. Azinphos-methyl use by county from 1990 through 1998

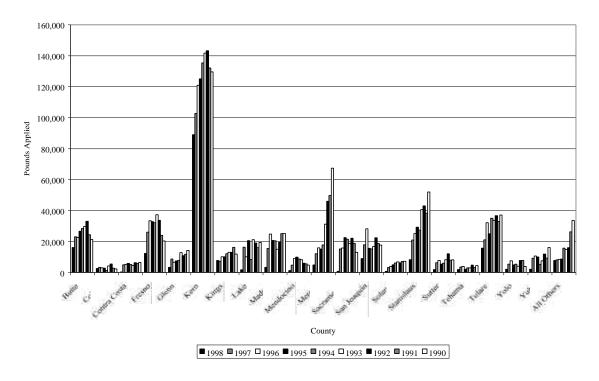
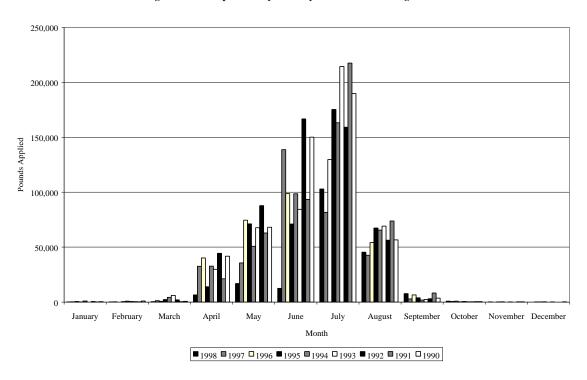


Table III-2 and Figure III-2 summarize azinphos-methyl use by month for 1990 through 1998. These data indicate that the period of peak use occurs from May through August, with more than 38 percent applied during the month of July.

Table III-2. Azinphos-methyl monthly use from 1990 through 1998.

	Pounds Applied								
Month	1998	1997	1996	1995	1994	1993	1992	1991	1990
January	72	295	503	98	963	32	456	104	412
February	81	171	44	382	788	538	327	268	970
March	329	1,273	656	2,310	4,355	5,940	2,022	344	680
April	6,547	32,589	40,185	13,905	32,669	29,752	44,391	21,223	41,689
May	16,796	35,622	74,631	71,140	50,778	67,673	87,713	62,830	68,006
June	12,483	138,771	98,705	71,126	98,526	84,448	166,786	93,489	150,046
July	102,928	81,657	129,749	175,359	163,141	214,500	159,197	217,587	189,893
August	45,352	42,550	54,189	67,435	65,430	69,106	56,266	73,806	56,541
September	7,601	2,853	6,410	3,860	1,779	2,370	2,941	8,197	3,541
October	692	508	842	277	461	261	246	393	337
November	57	8	128	195	42	67	10	254	194
December	41	56	56	144	3	62	0.13	11	229

Figure III-2. Azinphos-methyl monthly use from 1990 through 1998



Azinphos-methyl use by commodity or site for 1990 through 1998 is summarized in Table III-3. Although used on a wide variety of commodities, the highest use for this period was on almonds, walnuts, pears, apples, pistachios, and peaches (Figure III-3).

Table III-3. Azinphos-methyl use by commodity/site from 1990 through 1998.

	Pounds Applied									
Commodity/Site	1998	1997	1996	1995	1994	1993	1992	1991	1990	
Almonds	97,953	154,306	174,520	172,129	192,739	214,232	235,612	203,516	242,691	
Apples	13,418	36,225	39,057	37,714	36,737	43,960	46,497	46,774	51,767	
Berries/Small Fruits ^a	249	74	17	19	56	56	35	83	54	
Cole Crops ^b	2,296	2,293	1,280	509	1,014	635	680	102	445	
Field/Row Crops ^c	1,580	954	2,813	1,014	3,975	2,802	3,845	11,926	13,558	
Grapes	56	256	1,097	4,820	6,398	7,399	2,760	853	1,364	
Greenhouse/Nursery ^d	53	30	33	50	134	141	130	57	495	
Melons ^e	0	101	298	0	415	369	1,023	3,104	1,478	
Nectarines	506	841	1,559	2,848	2,484	2,537	3,285	3,151	3,155	
Peach	1,066	2,806	4,684	8,344	12,986	17,898	26,053	29,138	34,943	
Pear	6,047	50,162	48,829	70,142	56,069	69,281	66,174	57,164	57,469	
Pistachio	29,898	29,374	36,816	39,877	39,429	48,912	39,665	42,633	27,128	
Plums	1,058	1,513	1,739	1,439	1,634	3,564	5,825	4,325	4,696	
Pomegranates	151	172	517	482	371	422	366	206	0	
Potatoes	1,127	949	267	1,297	1,602	2,476	1,976	3,439	3,395	
Prunes	63	3,286	2,490	2,325	2,368	4,136	6,999	2,783	3,565	
Tomatoes	871	804	604	909	989	1,630	2,547	3,192	3,915	
Tree Fruits and Nuts	762	1,545	1,572	1,396	1,474	2,465	2,486	2,712	6,823	
Walnuts	35,655	50,614	87,882	60,906	58,049	51,292	74,392	63,332	54,917	
Other ^g	93	0.19	23	8	13	538	4	16	676.56	

^a Includes blackberries, raspberries, and strawberries.

^bBroccoli, brussels sprouts, cabbage, cauliflower, and chinese cabbage.

^cAlfalfa, artichokes, beans, celery, cotton, cucumbers, eggplant, oats, onions, peas, peppers, spinach, and wheat.

dIncludes Christmas tree plantations.

^eCantaloupes, honeydew/honey ball melons, watermelons, and other melons.

^fApricots, cherries, grapefruit, lemons, oranges, pecans, quinces, and tangerines.

ECOMMODITY and other fumigations, landscape maintenance, research commodities, rights of way, soil applications, and structural pest control

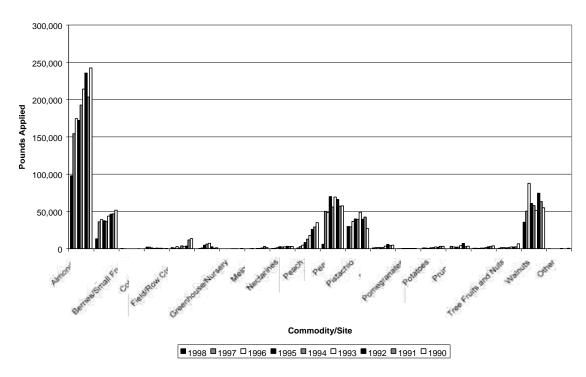


Figure III-3. Azinphos-methyl use by commodity/site from 1990 through 1998

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IV. Persistence and Fate in the Environment

$$H_3C \longrightarrow O$$
 $P \longrightarrow S \longrightarrow C$
 N
 N

Figure IV-1. Azinphos-methyl oxon

A. Persistence and Metabolic Fate in Plants

The studies summarized below describe the rate of degradation of azinphos-methyl from plant surfaces under dry conditions and after rain or irrigation events. The rate of formation and disappearance of the primary degradate, the oxygen analog (oxon; Fig. IV-1) is also discussed. The majority of the studies focused on measuring residues and did not propose mechanisms of degradation.

Azinphos-methyl is rapidly degraded from plant surfaces. Dislodgeable residues were typically less than 15 percent of the amount applied by 14 days after application. After 21 days, residues were less than 4 and 15 percent of the amount applied on Valencia orange leaf and fruit, respectively (Thompson, 1976). About 40 percent on the amount applied to grain sorghum was detected three days after application, 20 percent was present at six days, and less than 10 percent was present after 14 days (Dorough et al., 1966). Depending on the location of the sample relative to the direction of spray application, dislodgeable residues of azinphos-methyl on apple tree foliage decreased from 42 to 100 percent 14 days after spraying. This study was carried out under very humid conditions (Hall, 1975). Residues on apples decreased from 0.79 ppm immediately after application to 0.32 ppm 16 days later (Celik et al., 1995), with the loss attributed mainly to volatilization. About 40 percent of the pesticide volatilized from the surface of the fruit within 20 days, with very low losses attributed to solar irradiation and bacteria (1%).

Dislodgeable residues on the foliage of peach trees decreased from 444 ng/cm² immediately after application to 50 ng/cm² 14 days later (Bowman et al., 1982). These residues represented 73 to 89 percent of the total amount extractable. The percentage tended to decrease as the residues aged. Richards et al. (1978) found that dislodgeable residues persisted for 20 days (75 percent remaining) after an application of azinphos-

methyl to a peach orchard. However, the ambient temperature was much higher than normal for that date, the relative humidity was much lower than usual, and the orchards had not been irrigated for many weeks prior to application. For a previous study using the same site, pesticide concentration, formulation, and method of application, residues declined logarithmically to about 17 percent of the amount applied by day 13 post application.

The half-life of azinphos-methyl on cotton leaves was 2-4 days (Quinby et al., 1958). The rate of loss from leaves was reduced when oil was added to the spray mixture (Cole et al., 1986). For the first two days after application, higher residues were recovered from fields where no oil was used. By the fifth day, residues were about the same for both spray mixtures.

Miles et al. (1964) investigated the persistence of azinphos-methyl applied to forage. Residues declined from about 60 ppm fresh weight basis after application to about 2 ppm after 14 days. This decrease was compared to the theoretical dilution by growth alone, which is calculated as though the residue was an inert material and diluted based on plant weight at the time of spray and at the time of collection. It was concluded that plant growth is not a major cause of the decline of residues.

Residues are easily washed from leaf surfaces by rain or spray irrigation. The amount removed is proportional to the amount of rain and inversely proportional to the length of time between pesticide application and rainfall. Rain or spray irrigation easily removed ¹⁴C-azinphos-methyl from the leaves of bean plants, with the rate of removal appearing to depend on the intensity and time of rainfall after application (Steffens and Wieneke, 1975). Up to 68 percent on the radioactivity was removed from the leaf surface by five irrigation or rain events totaling 17.7 mm. Unmetabolized azinphos-methyl accounted for 90 percent of the removed activity. Two days after application, nearly 50 percent of the activity was removed by a relatively small amount of spray irrigation. Repeated wettings by rain may simultaneously stimulate uptake and metabolism of azinphosmethyl by the leaves. Increasing relative humidity increased the rate of uptake and metabolism.

Howell and Maitlen (1987) determined the effect of repeated overhead sprinkler irrigations on residues of azinphos-methyl on apple trees. A single irrigation one day post-application removed about 40 percent of the residue. A single irrigation six days post-application removed 22 percent of the dislodgeable residue. After a single irrigation

12 days post-application the residues were not significantly different from controls (not irrigated). With multiple irrigations, the residues removed by the second or third irrigation were similar to the losses on control trees. It was suggested that the initial irrigation removed the readily dislodgeable leaf surface residues, leaving residues that were more tightly bound to the leaf or absorbed by the leaf wax. Washing apples with distilled water removed 10 percent of the residues, whereas washing and peeling removed 72 percent (Celik et al., 1995).

Smith et al. (1983) found that the amount of azinphos-methyl lost in runoff (water and suspended sediment) from a sugarcane plot was dependent on the interval between application and rainfall. In the first year, losses were 0.08 percent of the amount applied. Seasonal rainfall was 655 mm and runoff was 18 mm. In the second year, losses were 0.55 percent of that applied. Rainfall was 322 mm and runoff was 34 mm. Losses did not correlate statistically with runoff amounts. The higher runoff in the second year was attributed to higher antecedent soil moisture and to shorter time intervals between insecticide application and runoff events. In the first year, no runoff occurred closer than 11 days after an application. In the second year, three runoff events occurred within five days after an application.

Following azinphos-methyl application to plants, the oxygen analog is formed and rapidly degraded. Kvalvag et al. (1976) reported the accumulation and disappearance of azinphos-methyl oxon in dislodgeable residues from orange tree leaves treated with a formulation that contained no detectable oxon. Oxon was found in dislodgeable residues from leaf surface samples collected 3 to 59 days after spraying. Oxon levels increased from $0.003~\mu g/cm^2$ on day 3, to a high of $0.057~\mu g/cm^2$ on day 17. Oxon levels decreased to a low of $0.014~\mu g/cm^2$ on day 59. It was reported that the values for the apparent oxon concentration versus time after spraying offer evidence for the transformation of azinphos-methyl to oxon, and that the oxon is then degraded under field conditions.

Average azinphos-methyl foliar residues decreased from 2.45 to 0.713 $\mu g/cm^2$ 6 days after an application to an apple orchard (Guthion 50WP; 1 lb a.i./acre). Residues were detected near the minimum detection limit (MDL) of 0.003 $\mu g/cm^2$ 77 days after application. The oxon was detected 72 hours after application at 0.082 $\mu g/cm^2$. Due to earlier applications, azinphos-methyl and the oxon were detected at 0.42 $\mu g/cm^2$ and 0.035 $\mu g/cm^2$, respectively, in pre-application samples (Maddy et al., 1985).

Edmiston et al. (1984) found that average leaf residues were 1.52 and $0.84 \,\mu\text{g/cm}^2$ at 7 and 28 days, respectively, after an application of azinphos-methyl to apple trees. No oxon residues were detected.

Maddy et al.(1984) found that degradation of dislodgeable residues on foliage did not decrease over a period of 14 days after peach orchards were treated with azinphosmethyl. The high levels of residue were detected at least 60 hours and as much as 14 days after application. The persistence was statistically correlated with high ambient temperatures (90 °F or above). Other factors, including the presence of low levels of previously applied fungicides, were not believed to influence residue levels. The highest average residue level from 1 lb a.i./acre applications was $1.56~\mu g/cm^2$ at 60 hours post spray. Oxon residues were not detected (MDL = $0.01~\mu g/cm^2$). For a 1.5~lb a.i./acre applications, the highest average residue level was $3.14~\mu g/cm^2$ at 7 days, and the highest average oxon concentration was $0.042~\mu g/cm^2$ at 14 days.

B. Persistence and Fate in Soil

The fate of azinphos-methyl in soil is influenced by its adsorption to soil, water solubility, and rate of degradation. Loss is predominantly through microbial degradation and volatilization. Azinphos-methyl does not leach to great depths in soil, even after soil incorporation or irrigation.

De Heer (1979) found that the soil adsorption coefficients of azinphos-methyl for various soils correspond well with the organic carbon content, and that adsorption increases with increasing organic matter content in the soil (Table IV-1).

Mobay (1985) summarized several studies of the fate and persistence of azinphos-methyl in soil and reported that it is strongly adsorbed to the surface of clay particles. With kaolinite clays, azinphos-methyl undergoes hydrolysis on the surface of the clay particles. For montmorillonite or silicate clays, it is adsorbed into the space between the layers of the clay.

Azinphos-methyl is susceptible to photodegradation in the soil environment. In incubating moist soil samples under fluorescent lights at 30 °C, the degradation half-life ranged from 10 days in clay soil to 80 days, in sand and loam (Mobay, 1985). Liang and Lichtenstein (1976) reported that photodegradation was inversely proportional to the organic matter content of the soil. In a loam soil with 4.7 percent organic matter, 84 percent of the azinphos-methyl remained; in a muck soil with 57 percent organic mater,

91 percent remained. Granular formulations were found to be more resistant to photodecomposition than liquid formulations (Mobay, 1985).

Table IV-1. Characteristics of soil and azinphos-methyl soil adsorption coefficient

% O.C. ^a	% Clay	CECb	Kď
5.05	53.3	389	70
9.29	64.3	487	149
15.43	59.8	623	409
· 11.63	55.5	570	211
4.04	27.7	250	53
5.92	33.8	. 313	7.7
	5.05 9.29 15.43 - 11.63 4.04	5.05 53.3 9.29 64.3 15.43 59.8 - 11.63 55.5 4.04 27.7	5.05 53.3 389 9.29 64.3 487 15.43 59.8 623 11.63 55.5 570 4.04 27.7 250

^a Percent organic carbon

Soil temperature and moisture also effect the rate of (Yaron, et al., 1974b). Sterile soil was used to eliminate the effects of microbial degradation. In a wet soil at 6 °C, the half-life was found to be 88 days. The half-life decreased to 29 days at 25 °C and 6 days at 40 °C. The same temperatures dry soil resulted in half-lives of 484, 135, and 36 days, respectively.

Two phases in the kinetics of azinphos-methyl persistence in soil were found (Yaron et al., 1974b). The first is a lag phase immediately after application when the initial concentration remains constant during a period of time. The lag phase was thought to be the time required for the development of an effective population of pesticide-degrading bacteria. This phase, however, was observed in both natural and sterile soil and may not be only of a biological origin. In the second phase, the rate of degradation follows first-order kinetics. The half-life was 135 days in dry, sterile soil and 13 days in moist, natural soil. The rate of degradation also increased with increasing temperature and soil moisture. The duration of the lag phase decreased with increasing temperature, particularly in dry soil. A 10 percent increase in temperature caused the disappearance of azinphos-methyl to start 11 days earlier in dry soil, and one day earlier in wet soil.

Azinphos-methyl does not leach through soil, even after incorporation or irrigation. Compared to a half-life of 12 days after the application of an emulsifiable concentrate formulation on the soil surface, the half-life was 28 days after incorporation of granular

^bCation exchange capacity, mmol/kg

^cSoil adsorption coefficient, cm³/g

formulation into the upper 4-5 inches of the soil (Schulz et al., 1970). One year after treatment, 13 percent of the applied amount was recovered in the form of azinphosmethyl and four degradates. Ninety to one hundred percent of azinphosmethyl recovered was in the top three inches of soil. Two years after application, only traces were found in the soil with none detected in a soil sample taken at six inches. Trace amounts (0.01-0.03 ppm) were found in the upper three-inch layer. Samples taken three and four years after application did not contain any residues. Similarly, Roberts et al. (1962) found that azinphos-methyl was not detected in the soil below six inches after three annual incorporations (18, 3, and 3 lbs. a.i./acre application rates). After three years, 0.2 lbs a.i./acre was present in the first six inches of soil. In a loam soil irrigated with large quantities of water by sprinkler irrigation (up to 592,000 gal/acre), azinphosmethyl was not transported deeply into the soil (Yaron et al., 1974a). Traces were detected in the soil at a depth between 12-30 cm, but none was detected below 30 cm. It was concluded that loss of azinphos-methyl from the 0-3.0 cm soil layer was probably due to decomposition or volatilization and not downward transport.

The persistence of azinphos-methyl in soil was studied for eight years after intentional gross topical contamination (Staiff et al., 1975). Experimental plots were subjected to natural elements: rain (approximately 25 cm per year), sunlight (over 275 days per year), temperatures (over 32 °C an average of 14 days each summer, and plots covered with snow approximately two months of the year). After contamination, the initial average concentration was 49,946 ppm at the 0-2.5 cm soil layer and 30,488 ppm at the 2.5-7.5 layer. By the end of the first year, concentrations in both levels had decreased to between one-half and one-third of the original values. From the second year and beyond, appreciable quantities remained in both levels. From the fourth through the eight year, the residue levels in the lower layer were consistently higher than in the upper layer. At the eighth year, the upper layer averaged 850 ppm while the lower level averaged 967 ppm. No azinphos-methyl was found below 30 cm.

The distribution and persistence of azinphos-methyl in a cranberry bog was investigated following three treatments at 1.1 kg a.i./hectare by chemigation (Wan et al., 1995). Sediment samples were collected were collected in the bog and at 3, 100, and 150 m along a ditch draining the bog. After the third chemigation, azinphos-methyl residues in bog sediment persisted for up to 210 days. The highest concentrations were 178, 650, and 1582 μ g/kg after each chemigation. Concentrations of 628 and 289 μ g/kg were found at 3 m and 100 m, respectively, 35 days after the first chemigation. These levels dropped to less that 30 μ g/kg at 255 days.

Azinphos-methyl is susceptible to microbial degradation. It is sensitive to decomposition by chitinoclasts, the group of bacteria that degrade chitin (Mobay, 1985). It is also degraded by soil bacteria that secrete enzymes, particularly phosphatases. Investigations have identified benzazimide, thiomethylbenzazimide, bis(benzazimidylmethyl)disulfide, and anthranilic acid as the principal end products of microbial degradation in soil (Engelhardt et al., 1984; Engelhardt and Wallnofer, 1983; Heuer et al., 1976).

C. Persistence and Fate in the Aquatic Environment

Numerous laboratory investigations have shown that degradation of azinphos-methyl increases with exposure to ultra-violet (UV) light, and increasing pH or temperature (Liang and Lichtenstein, 1972; Heuer et al., 1974; de Heer, 1979). The same findings have been made in simulated natural environments and in practical agricultural use.

Aqueous solutions of azinphos-methyl were exposed to UV (254 nm), yellow (589 nm), and red (656 nm) light. When exposed to UV light, degradation was rapid and extensive with complete degradation occurring after three hours of irradiation. Significant degradation did not occur with yellow or red light. Compounds identified after irradiation included anthranilic acid, benzazimide, N-methyl benzazimide, and methyl benzazimide sulfide. No mechanisms of photodegradation were proposed (Liang and Lichtenstein, 1972).

Degradation via hydrolysis increases with increasing temperature or pH (Table IV-2). At 25 °C, azinphos-methyl was relatively stable at pH 6 to 9. At pH 11, 97 percent was degraded. Azinphos-methyl was more stable as a deposit on a dry glass surface than on wet glass or in water (Liang and Lichtenstein, 1972; Heuer et al., 1974).

De Heer (1979) showed that the first-order hydrolysis conversion coefficients for azinphos-methyl, its oxygen analog, and the wettable powder formulation was dependent on temperature (Table IV-2). The wettable powder formulation showed a somewhat faster conversion than analytical grade azinphos-methyl, and the conversion rate of the oxygen analog was considerably higher than that of the parent compound.

The distribution and persistence of azinphos-methyl in a cranberry bog was investigated by Wan et al. (1995). Water was sampled from ditches draining the bog following three applications at 1.1 kg a.i./hectare by chemigation. The bog was normally surrounded by a dike system for water retention, but the water was allowed to flow from the reservoir

into a ditch during the study. Water samples were collected from various locations including in the bog and along a ditch draining the bog. It was found that azinphosmethyl residues persisted at least 72 days in water collected from the bog after the third chemigation. The highest concentrations were detected in the bog;114, 21, and 69 μ g/L, respectively, were detected one day after each of the three chemigation treatments. These levels decreased to 1.6 μ g/L two weeks after each of the first two chemigations, and to 0.2 μ g/l 72 days after the third. By 255 days after the first chemigation, it was not detected at any location (MDL = 0.05 μ g/L).

Table IV-2. Effect of temperature, pH, and formulation type on the hydrolysis half-life of azinphos-methyl.

Temp.		Half-life		
(°C)	pН	(days)	Reference	Comment
15	7.7	77	de Heer, 1979	
15	8.9	16.6		
20	7.6	55		
20	8.8	12.8		
25	7.6	16		
25	8.7	6.1		
6	8.6	36.4	Heuer et al., 1974	
6	9.6	4.95		
6	10.7	3.90		
25	8.6	27.9		
25	9.6	2.40		
25	10.7	2.00		
40	8.6	7.20		
40	9.6	0.65		
40	10.7	0.41		
10	6.7-8.1	624	de Heer, 1979	analytical grade
10	7.1-8.1	427		25% wettable powder
10	7.3-8.2	54		oxygen analog
20	5.7-7.5	109		analytical grade
20	6.1-8.4	91		25% wettable powder
20	7.4-8.3	16		oxygen analog

D. Residues Found in Air

Jeiger (1964a, 1964b) measured the concentration of azinphos-methyl in the breathing zone of workers during spraying and tank-filling operations. Air concentrations ranged from 0.05 to 2.55 mg/m³ (0.64 mg/m³ mean) for spraying operations, and from 0.26 to 6.2 mg/m³ (2.76 mg/m³ mean) for operations involving tank-filling. In the general work

area where formulators were using a 25 percent wettable powder formulation, respective minimum and maximum concentrations of 1.07 and 9.64 mg/m³ were detected.

Argauer et al. (1968) measured deposits of azinphos-methyl from an aerial application of an undiluted technical formulation (22% a.i.), and a diluted emulsifiable concentrate formulation (1.5% a.i.). The applications were conducted at two flight altitudes (2.4 and 9.1 meters) under adverse conditions (crosswind velocities of 6.5 to 16 km/hr) to produce the greatest magnitude of drift. Azinphos-methyl was applied at a rate of 0.28 kg a.i./hectare in two passes. The results are summarized in Table IV-3. Azinphos-methyl was detected as far as 800 m downwind.

Table IV-3. Azinphos-methyl concentrations (μg) detected downwind after aerial applications of undiluted technical (Technical) and diluted emulsifiable concentrate (EC) formulations. The applications were made to flight altitudes of 2.4 meters (FA 2.4) and 9.1 meters (FA 9.1).

Distance	FA 2.4	FA 2.4			
(meters)	Technical	EC	Technical		
60	47	37	270		
600	3.8	3.3	12		

Deposition of drift was measured after an application of azinphos-methyl to a cranberry bog (Wan et al., 1995). Guthion 2 SC® was applied at a rate of 1.3 kg a.i./hectare by sprinkler irrigation. The concentration of the drift deposits decreased with increasing distance from the outer perimeter of the sprinkler irrigation system. Aerial drift deposits were the equivalent of 1.3 and 0.3 gram per hectare at 0 and 1 meter, respectively. At 2, 4, 6, 8, 14, and 16 meters from the outer perimeter of the sprinkler system, drift deposits were the equivalent of 0.1 gram per hectare.

E. Documentation of Airborne Concentrations of Azinphos-methyl

The Air Resources Board (ARB) was requested by DPR to conduct an ambient air monitoring program for the pesticidal uses of azinphos-methyl. The monitoring program consisted of determining concentrations of azinphos-methyl in the ambient air of sites in populated areas (ARB, 1988), and in the vicinity of an application site (ARB, 1995).

1. Ambient Air Monitoring

Ambient air monitoring was conducted four days a week from June 22 through July 16, 1987 at five sites in Kern County. The background site was located at the ARB air monitoring station in Bakersfield. The monitoring was scheduled to coincide with expected applications to almond orchards. One site, Pond School, represented the "worst

case situation" because almond orchards were located directly to the east, south, and west less than 100 meters from the air sampler. The distance of samplers from orchards at the other sites was at least 400 meters. The monitoring results are summarized in Table IV-4. Maximum positive detections range from $0.028~\mu g/m^3~(2.2~ppt)$ at the Shafter School District Office and Bakersfield background site to $0.11~\mu g/m^3~(8.4~ppt)$ at the Pond School site. Over 69 percent of the total number of samples analyzed had no detectable residues (minimum detection limit = $0.022~\mu g/m^3$; 1.7 ppt for a 24-hour sample). Total azinphos-methyl use in Kern County from January through December 1987 was 154,665 pounds. Total respective use in Merced, Stanislaus, and Tulare Counties for the same reporting period was 65,671, 62,927, and 36,564 pounds (DPR, 1987).

Table IV-4. Summary of azinphos-methyl ambient air monitoring results in Kern County. Samples (24-hour) were taken over a four-week period from June 22 through July 16, 1987.

The ARB air monitoring station in Bakersfield was the background site.

			2 nd			#
	Maximum I	Maximum Positive		ositive	#	Above
Monitoring Site	^a μg/m ³	ppt^{b}	μg/m ³	ppt	Samples	$\mathbf{MDL}^{\mathfrak{c}}$
Pond School	0.11	8.4	0.06	4.6	22	11
McFarland						
Learning Center	0.053	4.1	0.04	3	30	10
Browning Road School	0.076	5.9	0.03	2.7	28	25
Wasco Fire Station	0.034	2.6	0.02	1.6	30	3
Shafter School District Office	0.028	2.2	ND^{d}	ND	30	1
Bakersfield	0.028	2.2	ND	ND	30	2

^a micrograms per cubic meter

parts per trillion

not detected

2. Application Site Monitoring

Application monitoring was conducted in July 1994 before, during, and for 72 hours after an application to a walnut orchard in Glenn County. Azinphos-methyl was aerially applied at the rate of 2 pounds of active ingredient per acre. The monitoring results are summarized in Table IV-5. Positive detections at each field sampling site occurred only during one sampling interval (during and one hour after application), and ranged from

minimum detection limit = $0.022 \mu g/m^3 (1.7 ppt)$ for a 24-hour sample

 $0.69~\mu g/m^3~(0.05~ppb)$ to $1.7~\mu g/m^3~(0.13~ppb)$. Nearly 87 percent of the total number of samples analyzed had no detectable residues (minimum detection limit = $0.08~\mu g/m^3$; 0.01~ppb for a 12-hour sample).

Table IV-5. Summary of air monitoring results in micrograms per cubic meter (µg/m³) and parts per billion (ppb) after an application of azinphos-methyl. Samples were collected in Glenn County during July, 1994 before, during, and for 72 hours after application.

	μ g/m ³ (ppb)									
Site	1	2	3	Sampling 4	Interval a	6	7	8	Maximum Positive	
East	ND ^b (ND)	1.5 (0.11)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	1.5 (0.11)	
West	ND (ND)	1.6 (0.12)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	1.6 (0.12)	
North - 1	ND (ND)	1.7 (0.13)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	1.7 (0.13)	
North - 2	ND (ND)	1.2 (0.09)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	1.2 (0.09)	
South - 1	ND (ND)	0.69 (0.05)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	0.69 (0.05)	
South - 2	ND (ND)	0.86 (0.07)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	0.86 (0.07)	
Maximum Positive	ND (ND)	1.7 (0.13)	ND (ND)	1.7 (0.13)						

a interval 1 = background on 7/28/94; interval 2 = during and 1 hour after application from 0600-0900 on 7/29/94; interval 3 = 7/29/94 from 0900-1030; interval 4 = 7/29/94 from 1030-1430; interval 5 = 7/29/94 from 1430-1930; interval 6 = 7/29-30/94 from 1930-0730; interval 7 = 7/30-31/94 from 0730-0730; interval 8 = 7/31-8/1/94 from 0730-0730

not detected, minimum detection limit = $0.08 \mu g/m^3$ (0.01 ppb) for a 12-hour sample

F. References

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